

JG13 Rec'd PCT/PTO 29 MAR 2001

FORM PTO-190 (REV. 12-29-99)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. 09/806346
INTERNATIONAL APPLICATION NO. PCT/DE 00/02723	INTERNATIONAL FILING DATE 05. August 2000	PRIORITY DATE CLAIMED 11. August 1999	
TITLE OF INVENTION Electrode and photoelectrochemical cell with four layers, method for producing a printable paste containing an electrolyte and/or carbon, and electrode			
APPLICANT(S) FOR DO/EO/US Dr. Georg Mermigdis, Rotkreuzstrasse 4, 73479 Ellwangen/Jagst, Germany			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11. to 16. below concern document(s) or information included:			
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information: 			

US APPLICATION NO. (37 CFR 2.101) 097/806346		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				860,00	
				ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860,00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	10-20 =	0	X \$18.00	\$ 0,00	
Independent claims	3-3 =	0	X \$78.00	\$ 0,00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$260.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 860,00	
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$ 430,00	
SUBTOTAL =				\$ 430,00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 430,00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$ 430,00	
				Amount to be:	\$
				refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>430,00</u> to cover the above fees is enclosed. Transfer to ABA number 021 030 004, ALC 13 10 0001					
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Dr. Georg Mermigidis Rotkreuzstrasse 4 D-73479 Ellwangen/Jagst Germany					
				<i>G. Mermigidis</i> SIGNATURE: Dr. Georg Mermigidis NAME _____ REGISTRATION NUMBER	

U.S. APPLICATION NO. (37 CFR 1.51) 097/806346		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY 860,00	
				\$ 860,00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	10-20 =	0	X \$18.00	\$	0,00
Independent claims	3-3 =	0	X \$78.00	\$	0,00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				\$	+ \$260.00
TOTAL OF ABOVE CALCULATIONS =				\$	860,00
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	430,00
SUBTOTAL =				\$	430,00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	+
TOTAL NATIONAL FEE =				\$	430,00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	+
TOTAL FEES ENCLOSED =				\$	430,00
				Amount to be:	\$
				refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>430,00</u> to cover the above fees is enclosed. Transfer to ABA number 021 030 004, ALC 13 10 0001					
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Dr. Georg Mermigidis Rotkreuzstrasse 4 D-73479 Ellwangen/Jagst Germany					
				SIGNATURE: <i>G. Mermigidis</i> Dr. Georg Mermigidis NAME	
				REGISTRATION NUMBER	

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United States of America

Dr. George Mermigidis, 05. August 2000, PCT/DE00/02723

Electrode and photoelectrochemical cell with four layers, method for producing a printable paste containing an electrolyte and/or carbon, and electrode

The invention refers to a procedure for manufacturing an electrolyte and/or carbon containing printable paste, in particular as electrode material for a photoelectrochemical cell, a procedure for manufacturing an electrode, in particular an electrolyte containing counterelectrode of a photoelectrochemical cell, as well as to an electrolyte containing electrode and a photoelectrochemical cell.

Dye sensitized photoelectrochemical cells are well known, which do have as a semiconductor a material with a very large energy gap, like titanium dioxide. A characteristic of such a semiconductor with a large gap is that it absorbs in particular the low energy part of the sunlight to a smaller extent. The sensitivity of such photoelectrochemical cells is increased by a dye layer, which is applied to the semiconductor layer.

The functions of light absorption and charge carrier separation, which take place in the case of conventional solar cells, like for example silicon solar cells, in only one material, are separated in such dye sensitized cells. The light absorption takes place essentially in the dye sensitized layer, also called as chromophore layer, while the charge carrier separation takes place at the boundary layer semiconductor/dye.

As dye for the sensitized layer a ruthenium (Ru) containing dye is preferred.

Suitable electrolytes for such photoelectrochemical cells are for example iodide, bromide, hydrochinon or other redox systems.

As electrode usually metal oxide semiconductors are used, in particular titanium oxide. A photoelectrochemical cell, as it is described above, is for example well known from the EP 0584307 B1.

Counter electrodes of carbon have been proved to be particularly favourable for photoelectrochemical cells. To get such counter electrodes carbon pastes are manufactured, which are applied to the appropriate substrate, for example TCO glass, and then annealed or burned, in order to get a stable layer.

The light absorbing layer, usually a TiO_2 -layer, can be sensitized only after burning or annealing the carbon paste, since the dye is temperature sensitive, and would therefore be destroyed in the process of burning or annealing. This has the consequence that for the sensitization much dye material is needed.

Therefore the purpose of the invention presented here is to make available an improved procedure for the production of a photoelectrochemical cell with a counter-electrode of carbon, as well as for the production of the material necessary for it and of an appropriate electrode and of a photoelectrochemical cell.

This purpose is reached with the procedures in accordance with the patent claim 1 as well as with an electrode in accordance with claim 3 and a photoelectrochemical cell in accordance with claim 6. The patent claims 2, 4 to 5, 7 to 9 and 10 represent particularly favourable features and kinds of realization.

According to the procedure of the invention presented here for manufacturing an electrolyte and/or a carbon containing printable paste, in particular as a electrode material for a photoelectrochemical cell, a solvent is supplied, which is mixed with electrolyte salts and electrolyte auxiliary.

1 to 30 weight % of carbon black with a large surface and/or conductivity carbon black and 1 to 30 weight % of graphite with very small electrical resistance are added to the solvent. The portion of weight depends on the electrolytic components used in each single case.

On principle the carbon containing paste can be manufactured on base of all suitable and also so far used electrolytes for the photoelectrochemical cell. Basically the carbon black or the graphite will not be in a functional interaction with the electrolytic components. Thus the invention is also applicable with electrolytes, which still can be developed in the future.

Thereupon the received suspension is agitated, in order to receive an essentially homogeneous distribution. Finally, the homogenized suspension is treated with ultrasound, so that a printable rigid paste develops.

The pastes can be characterized by impedance measurements.

Thus for the acquisition of necessary stiffness and printability of the paste according to the invention carbon is used that has a high agglomeration ability and a highly organized structure (fir tree), a large microscopic surface and a surface weight relation greater than $20 \text{ m}^2/\text{g}$, here called carbon black. As conductivity carbon black such carbon black is used that has a very high electrical conductivity, resistance values of max. $10^{-4} \Omega$ are acceptable.

Thus to decrease the electrical resistance of the paste according to the invention a type of carbon is used that has a small agglomeration ability and a low degree of structure (wooden peg), a small microscopic surface, but however a very small resistance in one direction, here called graphite. The resistance of the used graphite lies in the order of magnitude of $10^{-4} \Omega$, or less.

According to the invention's procedure, a printable rigid paste is made available, which has a consistency, which makes possible the application of the paste as an electrode or electrolyte respectively in a photoelectrochemical cell. In this procedure no burning or annealing is necessary. Therefore a thermal destruction of the dye is impossible, and the light absorbing layer can directly be sensitized with a dye layer. In that way the high loss of dye, which occurs due to the absorbing characteristics of carbon by using carbon electrodes, is avoided, so that for the sensitization less dye must be used, which leads to a clear reduction of costs.

It is further favourable that the quantity of electrolyte salt can be reduced. It was shown that a reduction down to 40 weight % of the original quantity in the pure electrolyte affects favourably the firmness of the paste.

Preferentially in the solvent the concentrations of the electrolyte salts and electrolyte auxiliary are in each case equal to those as they are used for the photoelectrochemical cell, in particular for the electrolytes in the solvent in a photoelectrochemical cell. As solvent in particular γ -Butyrolactone is used.

It proves to be favourable when about 10 weight % of carbon black with a large surface and/or of a conductivity carbon black are added. Likewise it proves to be favourable that about 8 weight % of graphite with a very small electrical resistance are added. Thus particularly high efficiencies of the photoelectrochemical cell can be obtained.

As carbon black with a large microscopic surface in particular Degussa carbon black F.W. 200 is suitable, as conductivity carbon black in particular Degussa carbon black XE2 is suitable. As graphite with a very small electrical resistance preferentially Timcal Timrex SFG 44 or Timcal Timrex SFG 75 is used.

In order to produce an essentially homogeneous suspension, the suspension with the added particles is preferentially stirred for 5 minutes and then treated in the ultrasound bath for 15 minutes with ultrasound. The length of the treatment with ultrasound depends on the irradiated performance and has to be executed so long until the paste indicates the desired consistency. The paste should not indicate fluidity and should be exclusively easily spread.

With a particularly preferred procedure ultrasound is irradiated with a power density of approximately 1 W/cm^3 on a paste with a volume of 20 cm^3 during a period of 15 minutes.

With the procedure according to the invention for manufacturing an electrode, in particular an electrolyte containing electrode of a photoelectrochemical cell, an electrolyte and/or a carbon containing, printable paste are supplied. The paste is applied and adapted to a substrate or a substrate network.

For the production of a photoelectrochemical cell the paste is directly applied to the porous light reflecting insulator layer, which covers the light absorbing layer which was sensitized with a dye layer, which is located on an electrode of the photoelectrochemical cell.

After applying the paste to and pressing the paste on the substrate the layer already has its operational status. Burning or annealing the layer, in order to get a fixed consistency, is not necessary, so that a very fast and thus economical procedure for the manufacturing of an electrolyte containing electrode is supplied.

Preferably, to the applied and pressed paste furthermore a graphite layer is applied, in particular by dusting on. Thus a thin, very conductive layer is made available. The graphite layer must be covering, so that a horizontal conductivity is given. One or two layers of graphite particles are sufficient. The thickness of the layer therefore depends on the particle size of the graphite particles, and in addition on the used method of dusting the graphite.

An electrolyte containing electrode according to the invention is used in particular as a electrolyte counterelectrode of a photoelectrochemical cell and comprises an electrolyte and/or carbon containing printable paste. This layer, which exists of the electrolyte and/or carbon containing paste, can be covered on one side with a further layer of dusted graphite. The electrolyte containing electrode is preferentially

manufactured in the same way as it is described above, the analogue applies to the electrolyte and/or carbon containing printable paste. The electrode can essentially completely be produced at ambient temperature, neither annealing or burning nor the following troublesome bubble free filling up with dye and electrolyte is necessary in connection with the application in a photoelectrochemical cell, so that the production process is substantially simplified and reduced in price.

The electrolyte containing electrode shows comparable quality characteristics with regard to conventional electrodes, so that no or only a very small performance or efficiency loss has to be expected with the application of the electrolyte containing electrode according to the invention in photoelectrochemical cells. The thickness of the electrode can be adapted to the desired aims, applied in photoelectrochemical cells the usual thickness lies between 10 to 100 μm , preferentially at 20 μm .

The electrode arrangement consists preferentially of a conductive layer and/or an insulating layer, the conductive layer can serve as an additional electrode item, while the insulating layer can be a shielding for the electrode arrangement or the photoelectrochemical cell.

An electrode, a diaphragm as isolation layer, an electrolyte counterelectrode and a with a dye layer sensitized light absorbing layer constitute a photoelectrochemical cell which according to the invention contains a counterelectrode and an electrolyte, which are realized in an integral manner and do consist of a layer of electrolyte and/or carbon containing printable paste. The carbon containing, printable paste is in particular manufactured in a procedure, as it is described above.

Such a photoelectrochemical cell has to be manufactured easily and inexpensive, without having to accept crucial losses of performance data, in particular a reduced efficiency of the photoelectrochemical cell, in comparison with conventional cells. The cost use value of a cell according to the invention is crucially improved by the electrolyte containing counterelectrode in relation to the state of the art.

A particularly favourable photoelectrochemical cell has an additional graphite layer on the carbon containing paste, which was dusted. Furthermore the electrode and/or the combination of counterelectrode and electrolyte are additionally covered with an electrically conducting layer. This electrically conducting layer can serve as electrode item and supply a particularly efficient electrode arrangement.

Preferred is the photoelectrochemical cell, in particular this one which has at least one electrically leading layer, which is covered with at least one insulating layer, which seal off the photoelectrochemical cell with respect to outward.

As a dye for the sensitized dye layer preferentially a ruthenium (Ru) containing dye is used. As a material for the conductive layers a metal, ITO or an electrically conductive glass turned out to be favourable.

The features and advantages according to the invention become particularly clear with the only attached figure (figure 1).

Figure 1 schematically shows a possible layer structure of an execution form of a photoelectrochemical cell according to the invention, in which an execution form of an electrolyte containing counterelectrode according to the invention is integrated.

In figure 1 a preferential execution form of the cell according to the invention cell 1 is represented. It has to be pointed out expressively that the shown layer thickness are represented not true to scale, and do only serve as explanation and representation of the principles of the structure.

With the photoelectrochemical four layer cell according to the invention, whose production is essentially characterised by four simple process steps, the individual layers are assembled as follows:

The first layer, the light absorbing layer (40), here titanium dioxide TiO_2 , which is applied to a electrically conductive carrier (10), here Indium Tin Oxide (ITO), is treated in a usual way with tertiary Butylpyridine or another Pyridinederivative. The TiO_2 - layer is porous and has a rough surface, to which a dye layer (50), also called as chromophore layer, is applied. In this implementation as dye a ruthenium containing dye is used. The combination of the TiO_2 - layer (40) and the dye layer (50) as described above are designated as light absorbing layer.

The second layer of the four layer cell consists of a light reflecting electrical insulation layer (80), which is applied to the light absorbing layer (40, 50) which is sensitized with a dye layer.

The third layer of the four layer cell, the electrode electrolyte combination layer (30) which consists of the electrolyte and/or carbon containing printable paste is directly printed onto the second layer and is pressed afterwards with a stamp into the insulation layer (80), with a pressure from approximately 100 to 50000 Pa (1 to 500 g/cm^2) in order to get thin layers. The paste (30) has a portion of 10 weight % Degussa carbon black F.W. 200 and a portion of 8 weight % graphite Timcal Timrex SFG 44. The paste is stirred for five minutes and then treated for 15 minutes with ultrasound before it is applied to the second layer, which is on the light absorbing layer (40, 50).

The fourth layer (31) of the four layer cell is a thin layer which consists itself of a few plies of graphite and which is made by dusting graphite onto the third layer, which comprises the electrolyte and/or carbon containing, printable paste (30).

The realisation of the four layer cell as shown in figure 1 contains an additional an ITO layer as electrical conductor (20).

The described photoelectrochemical cell is sealed off at both surfaces by an isolating layer (60) and (70) respectively. The isolating layers consist preferentially of a transparent material, like plastic or glass.

At least one of the isolating layers (60) and (70) must be permeable for the light, which has to be converted into electricity, so that the light can reach the light absorbing layer (40, 50).

In the implementation of a photoelectrochemical cell shown in figure 1 the insulating layer (60) is made of plastic, which is transparent for the light and is turned to the light, which has to be changed into electricity, and the insulating layer (70) is made of non-transparent plastic.

All the features of the invention that are revealed in the description above and in the drawing (figure 1) as well as in the requirements formulated before are both individually and in any combination substantial for the implementation of the invention.

Abstract

The invention relates to a method for producing a printable paste containing an electrolyte and carbon, in particular in the form of an electrode material for a counter electrode containing an electrolyte, for a photoelectrochemical cell. Said method consists of the following steps:

- preparing a solvent containing electrolytic salts and an electrolytic auxiliary;
- adding carbon black, e. g. with a large surface and/or a conductive carbon black;
- adding graphite, e. g. with a very weak resistance, so as to produce a suspension;
- stirring the solvent containing the carbon black and the carbon to produce a substantially homogeneous suspension;
- treating the homogenized suspension with ultrasound to produce a thick, printable paste.

Electrode and photoelectrochemical cell with four layers, method for producing a printable paste containing an electrolyte and/or carbon, and electrode

Patent claims

1. Procedures for manufacturing an electrolyte containing and/or carbon containing printable paste, in particular as electrode material for a photoelectrochemical cell, with the steps:
 - a) preparing a solvent containing electrolytic salts and/or an electrolytic auxiliary;
 - b) adding carbon black, e. g. with a large surface and/or a conductive carbon black and/or graphite, e. g. with a very weak electrical resistance, so as to produce a suspension;
 - c) stirring the solvent containing the carbon black and/or graphite to produce a substantially homogeneous suspension;
 - d) treating the homogenized suspension with ultrasound to produce a thick, printable paste
2. Procedures according to patent claim 1, characterized by the fact that in the solvent the electrolyte salts and the electrolyte auxiliary do exist in a concentration in each case, as it is used for an electrolyte in a photoelectrochemical cell, while as solvent preferentially γ -Butyrolactone is used, to which are preferably added 10 weight % of carbon black with a large surface of $20 \text{ m}^2/\text{g}$ or over and/or conductivity carbon black with an electrical resistance of max. $10^{-4} \Omega$ as well as 8 weight % of graphite with an electrical resistance of max. $10^{-4} \Omega$ and the received suspension is stirred for 5 minutes and then treated for 15 minutes with ultrasound.
3. Procedures for manufacturing an electrode, in particular an electrolyte containing electrode of a photoelectrochemical cell, which cover the following steps:
 - a) preparing an electrolyte and/or carbon containing printable paste, in particular a paste, which is manufactured in a procedure according to the claims 1 to 2;
 - b) applying and pressing the paste on a substrate or a substrate network, in particular on a, an electrode and at least one light absorbing layer containing, substrate network for a photoelectrochemical cell.
 - c) applying a graphite layer to the paste, preferably by dusting.
4. Procedures according to the claim 3, characterized by the fact that the paste is pressed with a material covered stamp on the substrate or the substrate network,

characterized by the facts that the substrate or the substrate network consists of a light reflecting electrical isolation layer of TiO_2 or that the electrical isolating properties of the substrate or substrate network are increased additionally by layers of cloth, paper or plastic foils.

5. Electrode arrangement in accordance with the claims 3 to 4, in particular an electrolyte containing counterelectrode arrangement of a photoelectrochemical cell, characterized by the fact that it comprises an electrolyte containing and/or a carbon containing printable paste, in particular manufactured in a procedure in accordance with one of the claims 1 to 2, which is characterized by the fact that it has a layer thickness from 10 to 100 μm , preferably a thickness of 20 μm .
6. Photoelectrochemical cell, which comprises:
 - a) an electrode,
 - b) a diaphragm as isolation layer
 - c) an electrolyte containing counterelectrode,
 - d) one with a dye layer sensitized light absorbing layer,

characterized by the fact that in the procedures mentioned in the claims 3 to 5 the counterelectrode and the electrolyte are realized in an integral manner and do consist of a layer (30) of a electrolyte and/or carbon containing printable paste, in particular a paste, which is manufactured according to one of the procedures mentioned in the claims 1 to 2.

7. Photoelectrochemical cell according to the claim 6, characterized by the fact that the electrolyte containing counterelectrode (30) contains a graphite layer, in particular a dusted graphite layer (31).
8. Photoelectrochemical cell according to the claims 6 or 7, characterized by the fact that the electrode (10) and/or the electrolyte containing counterelectrode (30, 31) are covered with an electrically conductive layer, metal, ITO or a conductive glass (10, 20) and that at least one of the electrically conductive layers (10, 20) is covered with an electrical insulating layer (60, 70) for which an isolating glass, an isolating plastic or other organic or inorganic materials are used.
9. Photoelectrochemical cell according to the claims 6 to 8, characterized by the fact that as dye for the light absorbing layer (40) a sensitizing dye layer (50) is used.
10. Module consisting of photoelectrochemical cells or other products which contain an electrolyte and/or a carbon containing printable paste, which was manufactured in a procedure according to the claims 1 to 2.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
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der PCT-Gazette verwiesen.

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(71) Anmelder und

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(54) Title: ELECTRODE AND PHOTOELECTROCHEMICAL CELL WITH FOUR LAYERS, METHOD FOR PRODUCING A
PRINTABLE PASTE CONTAINING AN ELECTROLYTE AND/OR CARBON, AND ELECTRODE

(54) Bezeichnung: ELEKTRODE UND PHOTOELEKTROCHEMISCHE VIERSCICHT-ZELLE SOWIE VERFAHREN ZUR
HERSTELLUNG EINER ELEKTROLYT- UND/ODER KOHLENSTOFFHALTIGEN, DRUCKFÄHIGEN PASTE UND ELEK-
TRODE

(57) Abstract: The invention relates to a method for producing a printable paste containing an electrolyte and carbon, in particular
in the form of an electrode material for a counter-electrode containing an electrolyte, for a photoelectrochemical cell. Said method
consists of the following steps: preparing a solvent containing electrolytic salts and an electrolytic auxiliary; adding carbon black,
e.g. with a large surface and/or a conductive carbon black; adding graphite, e.g. with a very weak resistance, so as to produce a
suspension; stirring the solvent containing the carbon black and the carbon to produce a substantially homogeneous suspension;
treating the homogenised suspension with ultrasound to produce a thick, printable paste.

(57) Zusammenfassung: Offenbart wird ein Verfahren zum Herstellen einer elektrolyt-, kohlenstoffhaltigen, druckfähigen Paste,
insbesondere als Elektrodenmaterial für eine elektrolythaltige Gegenelektrode für die photoelektrochemische Zelle, mit den Schrit-
ten: Bereitstellen eines Lösungsmittels, das Elektrolytsalze und Elektrolythilfsmittel enthält; Zusetzen von Ruß, z.B. mit großer
Oberfläche und/oder eines Leitfähigkeitsrußes und Zusetzen von Graphit z.B. mit sehr kleinem Widerstand, so daß eine Suspension
erzeugt wird; Rühren des den Ruß und den Kohlenstoff enthaltenden Lösungsmittels, so daß eine im wesentlichen homogene Sus-
pension erzeugt wird; Behandeln der homogenisierten Suspension mit Ultraschall, so daß eine druckfähige steife Paste entsteht.

WO 01/11702 A1

Declaration and Power of Attorney for Patent Application Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiernit an Eides Statt:

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Electrode and Photoelectrochemical Cell with four Layers,

Method for producing a printable Paste containing an

Electrolyte and/or Carbon, and Electrode

deren Beschreibung hier beigelegt ist, es sei denn (in diesem Falle Zutreffendes bitte ankreuzen), diese Erfindung

☒ wurde angemeldet am 08/05/2000
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Ich bestätige hiermit, daß ich den Inhalt der oben angegebenen Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Electrode and Photoelectrochemical Cell with four Layers,

Method for producing a printable Paste containing an

Electrolyte and/or Carbon, and Electrode

the specification of which is attached hereto unless the following box is checked:

☒ was filed on 08/05/2000
as United States Application Number or PCT
International Application Number
PCT/DE00/02723 and was amended on
 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

German Language Declaration

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Prior Foreign Applications
(Frühere ausländische Anmeldungen)

DE 199 37 910 A1 Germany
(Number) (Country)
(Number) (Land)

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Ich beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

(Application No.) (Filing Date)
(Aktenzeichen) (Anmeldetag)

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PCT/DE 00/02723 08/05/2000

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Priority Not Claimed
Priorität nicht beansprucht

08/11/1999
(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

pending

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

German Language Declaration

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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

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GR-60100 Katerini
Greece

Direct Telephone Calls to: (name and telephone number)

Dr. George Mermigdis Phone/Fax 0030351/35609

Vor- und Zuname des einzigen oder ersten Erfinders Dr. George Mermigdis	1-00	Full name of sole or first inventor Dr. George Mermigdis
Unterschrift des Erfinders <i>G. Mermigdis</i>	Datum 21.11.2001	Inventor's signature <i>G. Mermigdis</i>
Wohnsitz Agiou Dimitriou 72 GR-60100 Katerini Greece		Residence Agiou Dimitriou 72 GR-60100 Katerini Greece
Staatsangehörigkeit Greek		Citizenship Greek
Postanschrift Agiou Dimitriou 72 GR-60100 Katerini Greece		Post Office Address Agiou Dimitriou 72 GR-60100 Katerini Greece
Vor- und Zuname des zweiten Miterfinders (falls zutreffend)		Full name of second joint inventor, if any
Unterschrift des zweiten Erfinders	Datum	Second Inventor's signature
		Date
Wohnsitz		Residence
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(Im Falle dritter und weiterer Miterfinder sind die entsprechenden Informationen und Unterschriften hinzuzufügen.)

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**STATEMENT CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(b))--INDEPENDENT INVENTOR**

Docket Number (Optional)

Applicant, Patentee, or Identifier: Dr. George MermigidisApplication or Patent No.: PCT/DE 00/02723Filed or Issued: 05. August 2000Title: Electrode and photoelectrochemical four-layer cell as well as procedure for the production
of an electrolyte- and or carbon containing, printable paste and a electrode

As a below named inventor, I hereby state that I qualify as an independent inventor as defined in 37 CFR 1.9(c) for purposes of paying reduced fees to the Patent and Trademark Office described in:

- ☐ the specification filed herewith with title as listed above.
- ☒ the application identified above.
- ☐ the patent identified above.

I have not assigned, granted, conveyed, or licensed, and am under no obligation under contract or law to assign, grant, convey, or license, any rights in the invention to any person who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

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Separate statements are required from each named person, concern, or organization having rights to the invention stating their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

Dr. George Mermigidis

NAME OF INVENTOR

NAME OF INVENTOR

NAME OF INVENTOR

G. Mermigidis

Signature of inventor

Signature of inventor

Signature of inventor

12. January 2001

Date

Date

Date

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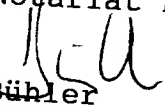
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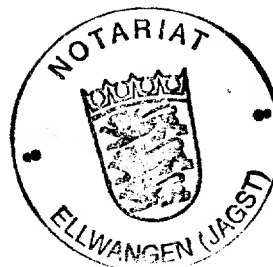
Herrn Dr. George Mermigidis,
Rotkreuzstr. 4, 73479 Ellwangen,
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6. am

19.02.01

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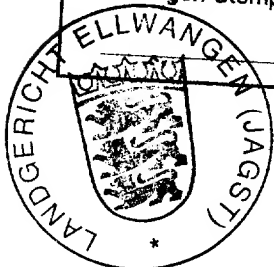
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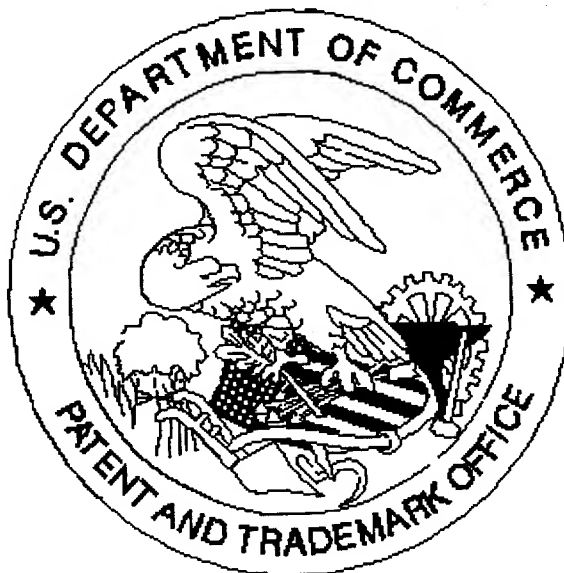
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